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SOLUBLE PHOTOGRAPHIC LAYERS OF COLLOIDAL GUMS AND PROCESS OF CONDITIONING SUCH GUMS FOR SUCH USE

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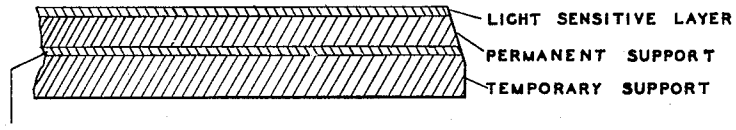


LAYER OF CARAGEEN EXTRACT OF LICHEN OR PSYLLIUM SEED WHICH HAS BEEN HYDROLYSED BY AN ACID OR ENZYME UNTIL THE COLLOID IS SOLUBLE IN A PHOTOGRAPIC BATH AND WHEN CAST YIELDS A TRANSPARENT NON-STICKY LAYER

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## SOLUBLE PHOTOGRAPHIC LAYER OF COLLOIDAL GUMS AND PROCESS OF CONDITIONING SUCH GUMS FOR SUCH USE

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The present invention relates to soluble photographic layers prepared from colloidal gums, said layers having adhesive properties, a method of conditioning said gums for use in making said layers and the gums so conditioned.

Colloids are extensively used in photography in the manufacture of layers such as surface-, back-, and anti-halation layers and adhesive layers. In the latter case they are extensively employed in the formation of the so-called photographic strip film. Such film, as known, essentially comprises, in the order of their arrangement, a temporary support, a strip or adhesive layer, a permanent support and a photographic emulsion. The prior art has proposed to utilize for this purpose such colloids as soluble gelatine, glues, dextrines and the like. Inasmuch as such colloids are naturally of an adhesive character, they may also be employed for the formation of the other layers previously mentioned, the character or property in question permitting them when cast into layers, to be united directly to the film base or other layers thereon. Such substances have certain disadvantages when used in these relationships. In the co-pending application of Duerr et al., Serial No. 285,498, filed July 20, 1939, entitled "Photographic strip film and photographic strip film paper," now U. S. P. 2,275,617 it was proposed to overcome these disadvantages, particularly in the manufacture of adhesives for strip film, by employing in lieu of said colloids certain vegetable mucilages and pecto-celluloses. It was found that these substances exhibited the peculiar property of having the viscosity thereof greatly diminished by photographic fixing baths, particularly those containing sodium thiosulphate, so that when strip film containing the same was immersed in such baths, the bond between the temporary support and the permanent support was destroyed. It was further noted in that application that this property is not common to all colloids and in this connection reference was made to carageen (*Chondrus crispus*), agar-agar, extracts of lichen (*Cetraria icelandica*) and extracts of psyllium seed (*Plantago psyllium*). These substances, though possessing good swelling properties, dissolve too slowly to permit their use for adhesive layers or for the soluble layers previously mentioned. No particular reason is known as to why this difference in characteristics of the two classes of gums exists. Thus from a chemical standpoint, there is a relatively close similarity therebetween. For instance, the building units of both consist mainly of hexuronic acids or similar carbohydrate-like substances. Another characteristic which they possess in common is that they yield mucic acid upon oxidation. On the other hand, it is true, that the internal structures in many of the substances of the classes vary in the arrangement of their molecules from one class to another. Variations also appear between substances of the same class. This is in part attributable to the fact that these products are obtainable from different sources, the best known example of this being agar-agar. Moreover some of the gums contain only carbohydrates, whereas others may also contain proteins and fats.

Despite the absence of an explanation or particular reason for the noted difference between the two groups of colloids, I have now discovered that the group involving carageen, extracts of lichen and extracts of psyllium seed can be conditioned for use in the above relationships and with the same advantage as the class of colloids mentioned in said application Serial No. 285,498. The purpose and object of the present invention are, therefore, the processing of said colloids to condition them for use by increasing their solubility without impairing their viscosity too greatly, the conditioned colloids and the use thereof as the adhesive in photographic strip film.

The conditioning treatment to which reference has been made involves a partial hydrolysis of the colloids in question either by acids, mineral or organic, or by enzymes. The hydrolysis leads to products of much greater solubility than the original colloids and of sufficient viscosity to serve the desired purpose. Suitable acids for the hydrolysis are hydrochloric acid, sulfuric acid, acetic acid, formic acid, propionic acid and the like. Suitable enzymes are the products sold by Roehm & Haas Co. of Philadelphia, Pa., under the trade-names "Orthozyme X" (activated trypsin) and "Pectinol 100," the product marketed by Eimer & Amend under the trade-name "Amylopsin" and the enzymes pepsin, trypsin, pancreatin, rennin (from rennet), pectinase, diastase and the like. The degree of solubility effected will depend on the extent of the hydrolysis and the agent employed and may be adjusted to fit the requirements of any particular case. Because the extent of hydrolysis will depend upon the agent used and the use to which the colloid is to be put, it is impossible to give a specific statement of a time of reaction which is applicable in all cases. It may be said, however, that the treatment must produce a product readily soluble in photographic treating baths. In certain cases this may also mean solubility in water, but this is

purely incidental. On the other hand, the time of treatment must not proceed so far as to result in products sticky in character. The duration of reaction is, therefore, at least to an extent, that products soluble in photographic treating baths result but is not so prolonged that sticky products ensue. A simple test will enable an operator to determine when he is within these limits and hence the fact that a specific time statement cannot be given is of no consequence.

Acids either organic or inorganic serve to catalyse hydrolytic reactions independently of the nature of the material hydrolysed or of the bonds to be hydrolysed. They accelerate hydrolysis of carbohydrates, proteins or fats uniformly, the degree being dependent to a certain extent at least upon the duration of their action. The same does not apply to the action of enzymes. Their action is specific as regards the material treated, different enzymes being required for carbohydrates, proteins or fats. Consequently by a proper selection of or by a combination of proteolytic or carbohydrate splitting enzymes, the colloids may be converted into products different in character from those obtained by the treatment with acids. For instance, the application of a carbohydrate splitting enzyme (diastase) may leave the protein component entirely intact, such component, as is known, being important for the adhesive strength of the colloid layer. On the other hand, the application of a protein hydrolyzing enzyme (trypsin) may leave small amounts of suspended particles of fat unaffected, the destruction of which by acid hydrolysis would eliminate a desirable self-lubricating effect of the layers. The choice of the enzyme is, therefore, dictated, on the one hand, by the constitution of the colloid, and on the other hand by the properties which the operator desires in the final product.

It is to be pointed out that in general the acid hydrolysis produces a rapid decrease in viscosity and, therefore, care must be taken if products of high molecular weight are to be retained. On the contrary, the decrease in viscosity produced by enzymic hydrolysis is more easily controlled and less difficulty is involved in producing products of the desired viscosity. By using either one or a combination of the methods, the hydrolysis may be carried to such an extent that products of the desired viscosity, swellability and solubility may be obtained.

The invention is further exemplified by the accompanying self-explanatory drawing and the following examples, but it is to be understood that the examples are merely illustrative of the invention. The drawing illustrates in section strip film containing a colloid treated according to the invention as the adhesive layer.

*Example 1.*—A complete extract of 5 kg. of carageen is made with 100 liters of 3% acetic acid at room temperature. The solution is filtered and then heated to 100° C. and thereafter quickly cooled. The solution may be cast as in Examples 1 and 2 to produce either an adhesive layer or an anti-halation coating, or the like. The cast film is easily soluble in developers, fixers or water but possesses sufficient adhesion to prevent premature stripping.

*Example 2.*—5 kg. of psyllium seed are extracted with 100 liters of boiling water for 2 hours and filtered while hot. 2 liters of glacial acetic acid are added to the filtrate which is then kept for 20 to 30 minutes at a temperature of 90 to 95° C. After cooling the solution is neutralized with sodium carbonate. The solution may then be cast as in Examples 1 and 2. The film obtained by casting is soluble in developers, fixers or water but is of such adhesive strength that premature stripping is avoided.

*Example 3.*—5 kg. of Iceland moss are extracted with 100 liters of a 1% solution of potassium carbonate at a temperature of 90 to 95° C. The extract is filtered off and the residue washed with water. The extract is discarded. The residue is again extracted for 2 hours with 100 liters of 5% acetic acid at a temperature of 90 to 95° C. and filtered. The acid extract forms a semi-transparent film soluble in water, insoluble in developers but soluble in fixers. The solution may be used to form the layers previously mentioned.

*Example 4.*—A 5% solution of agar-agar, disinfected with phenol, is buffered to pH 4.5 with McIlvaine buffer. (Handbook of Chemistry and Physics. 16 edition, p. 577.) 250 mg. per liter of the product sold by the Roehm & Haas Company of Philadelphia, Pa., under the trade-name "Pectinol 100" are added and the solution kept in an incubator for 48 hours at 45° C. The pH is then increased to 7.5 whereupon 250 mg. per liter of the product sold by Roehm & Haas under the trade name "Orthozyme X" are added and again the solution held in the incubator for 72 hours. After removal from the incubator, the solution is heated to 90 to 95° C. to stop the action of the enzymes. The solution is filtered while hot from undissolved particles and may then be used in strip film, surface- and anti-halation coatings and the like.

*Example 5.*—2 kg. of carageen are completely extracted with 100 liters of warm water and the extract filtered. 100 g. of rennin 1:30,000 are added to the non-buffered solution and kept in the incubator at 40° C. for 40 hours. Thereafter the solution is heated to 90–95° C. to stop the action of the enzyme and filtered. It serves as an excellent adhesive for strip film, or for surface and anti-halation coatings. Instead of rennin, the same amount of the product sold under the trade-name "Amylopsin" with a small amount of sodium pyrophosphate as an activator may be used with similar results.

*Example 6.*—5 kg. psyllium seed (*Plantago psyllium*) are extracted with 100 liters of boiling water for 2 hours. After cooling a mixture of 50 g. of rennin 1:30,000 and 50 g. of the product sold under the trade-name "Amylopsin" are added with a small amount of sodium pyrophosphate. The solution having a pH of 7.5 is kept in the incubator for 40 hours at 40° C.

Adhesive layers made of this solution are extremely soluble in photographic fixing solutions. This solution may also serve for surface and anti-halation coatings.

*Example 7.*—1 kg. of Iceland moss (*Cetraria islandica*) are submersed in 20 liters of water and autoclaved for 2 hours at a pressure of 10–15 pounds per sq. m. After cooling, 50 g. of "Pectinol 100" are added and after the pH has been adjusted to 4.5 with McIlvaine buffer, the solution is kept in the incubator at 40–45° C. for 24 hours. Thereupon the pH is increased to 7.5 and after 50 g. of "Orthozyme X" have been added the solution is returned to the incubator and kept there for 48–64 hours at 40° C.–45° C. After the incubator treatment the extract is heated to 90° C. and filtered while hot.

An adhesive made with this solution is easily

soluble in developers, insoluble in fixers, but soluble in water subsequent to fixation and allows easy stripping. The solution may also serve for surface- and anti-halation coatings.

What I claim is:

1. A photographic strip film comprising a permanent support having a silver halide emulsion thereon and a temporary support containing as the adhesive layer between the temporary and permanent supports the hydrolyzed colloid prepared by subjecting a colloid selected from the class consisting of carageen, extract of lichen and psyllium seed to hydrolysis by means of a hydrolysing agent selected from the class consisting of acids and enzymes while heating until the colloid becomes readily soluble in photographic baths and when cast forms a transparent non-sticky layer.

2. The photographic strip film of claim 1, wherein the hydrolyzed colloid is prepared by means of an acid.

3. The photographic strip film of claim 1, wherein the hydrolyzed colloid is prepared by means of an enzyme.

4. The photographic strip film of claim 1 wherein the hydrolyzed colloid is carageen.

5. The photographic strip film of claim 1 wherein the hydrolyzed colloid is carageen and wherein the same is prepared by means of acetic acid.

6. The photographic strip film of claim 1 wherein the hydrolyzed colloid is extract of lichen.

7. The photographic strip film of claim 1 wherein the hydrolyzed colloid is extract of lichen and is prepared by means of an acid.

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